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Template Synthesis and Micellization of Block Copolymers with Interacting Blocks

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It is known that A-B and A-B-A block copolymers with interacting blocks are related to the class of intramolecular polycomplexes. Such block copolymers form a stable micellar structures in dilute aqueous solutions due to hydrophobic interactions between non-polar bound segments of the blocks. Given micellar structures have attracted a considerable attention due to their possible applications as different templates, drug delivery systems, nanoreactors. Here we presented peculiarities of a template synthesis of the block copolymers consisting interacting poly(ethylene oxide) and poly(acrylic acid) blocks and also its self-assembly to micelles in acidic aqueous solutions, which was confirmed by Transmission Electron Microscopy (TEM).

Keywords: Block Copolymer, Template Synthesis, Dynamic Matrix Effect, Intramolecular Polycomplex, Self-Assembly, Micelles

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1. INTRODUCTION

Heterogeneous polymers, particularly block- and graft copolymers, are considered as perspective functional materials. They are widely used as variable templates, drug delivery systems, solid polymeric electrolytes and in many others nanotechnologies processes [1, 2]. The application of these copolymers in modern nanotechnologies requires improving the strategy of their synthesis for obtaining of the products with controlled molecular weight, polydispersity and architecture.

In the present work a template synthesis of the block copolymers containing chemically complementary poly(ethylene oxide) and poly(acrylic acid) with a different chain lengths of the both blocks were studied. It has been shown that the products of similar template syntheses are block copolymers, which form intermolecular polycomplexes (IntraPCs) [1]. According to our previous studies, block copolymers based on poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAAc) form IntraPCs in acidic solutions [3]. At low pH the polyacid blocks were protonated and interacted with PEO blocks that resulted in an intense micellization initiated by hydrophobic interactions between non-polar bound segments of the blocks. This special type of micelles contains hydrophobic "core" with H-bonded segments of interacting blocks and hydrophilic "corona" with free (unbound) segments of longer blocks. Here we demonstrate the morphology of the micelles that were obtained in acidic solutions of the synthesized block copolymers. The average micelles size was indicated by TEM.

2. EXPERIMENTAL SECTION

2.1 Materials and synthesis

A-B and A-B-A di- and triblock copolymers consisting poly(ethylene oxide) block and block or blocks of poly(acrylic acid) with a variable length of the both blocks were synthesized by a radical block copolymerization process. Methoxypoly(ethylene oxide) (M_{vMOPEO} = 1.1 – 5.3 kDa) from "Fluka" (USA) and poly(ethylene oxide) (M_{vPEO} = 6 kDa) from "Aldrich" (USA) were used correspondingly in the A-B and A-B-A block copolymerization processes. Terminal hydroxyl groups of MOPEG/PEG were activated by cerium ammonium nitrate from "Aldrich" (USA) as was described earlier [1, 3]. The molar ratio [Ce^{IV}]/[-OH] = 1 was constant in all syntheses. The concentration of acrylic acid (AAc) from "Fluka" (USA) in the reaction mixtures was changed from 0.35 to 2.0 mol$_{AAc}$/base-mol$_{MOPEG(PEG)}$). The reagents were mixed in the deionized water and inert atmosphere at 25 °C for 24 h. The processes were accompanied by a phase separation. The sediments of DBCs and TBC in H-form were rewashed by the deionized water after syntheses and transformed to Na-form by dissolution in water with sodium hydroxide. A pure PAAc was obtained by a free radical homopolymerization of AAc in the same experimental conditions at the presence of ethanol instead MOPEG/PEG ([AAc]/[EtOH] = 0.35÷2). The (co)polymerization rate and the monomer conversion in the both processes were controlled by potentiometric titration. A certain volume of the reaction mixture (~2 ml) was taken through a definite time of the process. Potentiometric titration of the non-reacted AAc was performed by 0.2 N NaOH in an inert atmosphere at T = 25±0.1 °C using a 1-160M pH-meter (Belarus) calibrated with standard buffers.

2.2 Results and discussion

The essential increase in the (co)polymerization rate and the monomer conversion during the PAAc block copolymerization process with MOPEG as compared to

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AAc homopolymerization was observed at relatively low monomer concentrations ($C_{AAc} < 1.46$ mol·dm^{-3}), pointed out the positive dynamic template effect (Fig. 1 a, b, c, d). The value of the dynamic template effect grew with increase in MOPEO block (matrix) length at similar low monomer concentration ($C_{AAc} = 0.73$ mol·dm^{-3}) in reaction mixture (Fig. 1 **a, b, c**). At the $C_{AAc} = 1.46$ mol·dm^{-3}, the kinetic curves for both the processes were drawn together, thus implying disappearance of the positive dynamic template effect (Fig. 1 f).

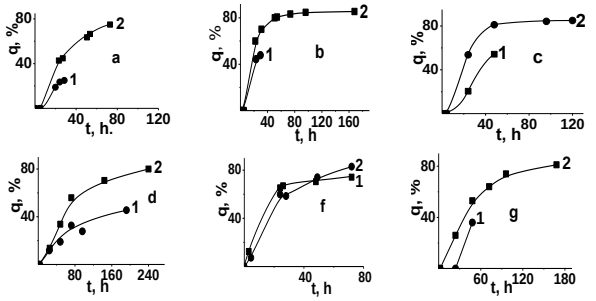


Fig. 1 – The time–conversion curves for the homopolymerization -*1* and PAAc block copolymerization -*2* with MOPEG (a, b, c, d, f) and PEG (g). $M_{vMOPEG} = 1.1$ (a), $M_{vMOPEG}=2.0$ (b), $M_{vMOPEG}=5.3$ (c, d, f), $M_{vPEG}=6.0$ (g) kDa; AAc concentration: 0.73 (a, b, c), 0.37 (d), 1.46 (f), 0.52 (g) mol/dm^3. T = 20 °C

The kinetic parameters of both processes, which were calculated from Fig. 1, are shown in the Table 1. Note, that the rate of both processes significantly increased with the growth of the monomer concentration.

Table 1 – Kinetic parameters of homopolymerization and block copolymerization

№	Sample	C_{AAc}, mol /dm^3	$M_{vMOPEO/PEO}$ kDa	$V_p^{20} \cdot 10^{6}$ a) mol/(dm^3·s)	q b), %
a	DBC1	0.73	1.1	4.9	49 (1)
	PAAc			2.8	25 (1)
b	DBC2	0.73	2.0	6.6	67 (1)
	PAAc			4.8	47 (1)
c	DBC3	0.73	5.3	5.6	81 (2)
	PAAc			2.4	54 (2)
d	DBC4	0. 37	5.3	0.86	72 (2)
	PAAc			0.47	34 (2)
f	DBC5	1.46	5.3	10.72	73 (2)
	PAAc			10.99	71 (2)
g	TBC	0.52	6.0	1.6	53 (2)
	PAAc			2.0	36 (2)

a) The rate of (co)polymerization at the monomer conversion equaled to 20 %.
b) The monomer conversion in 28.5 (1) and 48 (2) hours after the (co)polymerization beginning

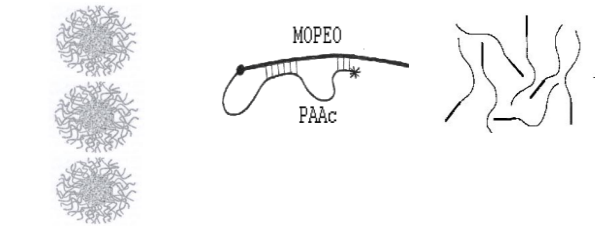
The essential increase of the monomer conversion during the PAAc block copolymerization process with PEG as compared to AAc homopolymerization pointed out the template effect too (Fig. 1 g). In this case the significant initial inductive period for AAc homopolymerization was present, but the rate of homopolymerization after inductive period was practically the same as the analogous rate of PAAc copolymerization (Table 1).

Thus, it was revealed that the PAAc block copolymerization process with MOPEG/PEG had the template character only at a relatively low monomer concentration in the reaction mixture ($C_{AAc} < 1.46$ mol·dm^{-3}). When the monomer concentration in the reaction mixture turned out higher than 1.46 mol·dm^{-3}, the rate of copolymerization process was increased so strongly that the growing PAAc chains had not enough time to interact with the template blocks of MOPEO. According to the studies [1, 4] the template effect is caused by the formation of the H-bond system between the propagating ("daughter's") PAAc chains and MOPEO/PEO blocks.

2.3 Micellization of DBCs and TBC in water

The template character of the block copolymerization process pointed out the existence of the intramolecular polycomplexes in DBC_{PAAc} and TBC_{PAAc} macromolecules in H-form due to formation of H-bonds between growing PAAc chains and MOPEO or PEO blocks [1, 4].

According to our study [3], a self-assembly of the copolymer macromolecules due to: i) IntraPC formation and ii) hydrophobic segregation indicated in aqueous copolymer solutions at the pH ≤ 4. At the same time, the IntraPC formation and micellization is impossible in the case of fully deprotonated copolymers. A scheme of the micellization process for DBCs is represented:



Micelles of DBC_{PAAc} (pH ≤ 4) | Partially destructed IntraPCs (4 < pH < 6) | Separate DBC_{PANa} (pH ≥ 6)

Specific construction of the micelles in the case of asymmetric block copolymers with chemically complementary components was discussed below.

2.4 The micelle characterization by transmission electron microscopy (TEM)

TEM images of DBCs and TBC micelles were recorded with a JEM-I23O instrument ("JEOL", Japan) operating at an accelerating voltage of 90 kV. Small drops (~$1 \cdot 10^{-4}$ cm^3) of DBCs and TBC solutions ($C_{BC} = 0.5$ - 1 kg·m^{-3}) at pH = 2.5 was deposited in copper grids coated with Formvar film and carbon and then were dried for ~ 1-2 min at a room temperature. Electron images were obtained in 24 hours' time after the sample preparation.

The molecular characteristics of DBCs and TBC samples with the different relative length of the blocks that were used in this experiment are shown in the Table 2. According to data in Table 2, the ratio between PANa and MOPEO units for DBC4 was equal to 1. So the DBC4 sample contained smaller excess of unbound units of PAAc block.

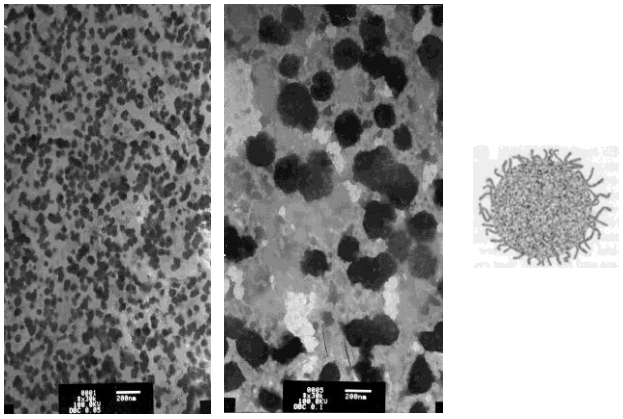
Table 2 – Molecular parameters of block copolymers

Sample	$M_{nMOPEO/PEO}$ kDa	M_{nPANa} kDa	$M_{nDBC/TBC}$ [a] kDa	n [b]
DBC4	5.3	12.1	17.4	129/120
DBC5	5.3	23.1	28.3	245/120
TBC	6.0	7.6	21.2	81/136

[a] $M_{nDBC}=M_{nMOPEO}+M_{nPANa}$, $M_{nTBC}=M_{nPEO}+2\cdot M_{nPANa}$.
[b] The ratio between units of PANa and MOPEO/PEO

One could be assumed that macromolecules of DBC4 formed spherical "crew-cut" micelles [5] contained a large hydrophobic "core" with H-bonded segments of the blocks and a short "corona" with free nonionic segments of PAAc blocks. The alternative micellar structures could be attributed to DBC5 and TBC, which contained a significant excess of unbound units of PAAc or PEO blocks (correspondingly for DBC5 and TBC). In the case for DBC5 and TBC the formation of "hairy-type" micelles with relatively small hydrophobic "core" and a large "corona" would be expected [2, 5].

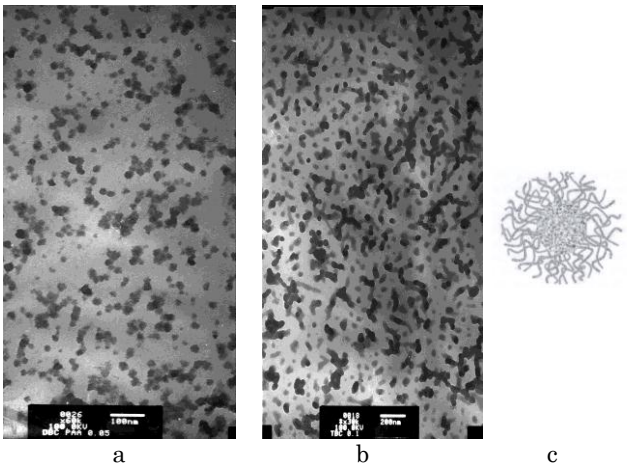
TEM images of real DBCs and TBC micelles that were obtained in acidic solutions with copolymer concentrations above CCM [3, 5] are represented in Fig. 2, 3.



a **b** **c**

Fig. 2 – TEM images of micelles for $DBC_{PAAc}4$, C_{DBC} = 0.5 (**a**), 1 kg·m^{-3} (**b**) at pH=2.5, schematic representation of a "Crew-cut" micelle (**c**).

It was shown that DBCs and TBC micelles contained a dense hydrophobic "core" and developed "corona". Note that a micelle shape differed from spherical one in many cases (particularly for DBC5 and TBC). Well known that the size of micelles is depended from the copolymer concentration [2, 5]. A sizes of DBC4 micelles were equal to 41÷82 nm in the acidic solution with C_{DBC4} = 0.5 kg·m^{-3} and were increased in ~4 times (156÷313 nm) to solution with C_{DBC4} = 1 kg·m^{-3} (Fig. 2 a, b). DBC5 and TBC micelles, which contained significant larger developed "corona" (Fig. 3), had more small sizes than DBC4 micelles. A sizes of DBC5 micelles to 5 ÷ 32 nm (for C_{DBC} = 0.5 kg·m^{-3}) and of TBC micelles to 20÷94 nm (for C_{TBC} = 1 kg·m^{-3}) were indicated.



a **b** **c**

Fig. 3 – TEM images of micelles for $DBC_{PAAc}5$, C_{DBC} = 0.5 kg·m^{-3} (**a**), TBC_{PAAc}, C_{TBC} = 1 kg·m^{-3} (**b**) at pH=2.5, schematic representation of a "Hairy-type" micelle (**c**)

3. CONCLUSIONS

Processes of block copolymerization of PAAc with MOPEG/PEG have a template character because the formation of the H-bond system between the propagating ("daughter's") PAAc chains and MOPEO/PEO blocks. Template effects of given syntheses were depended on the monomer concentrations in reaction mixture. The positive dynamic template effects in the DBCs and TBC syntheses at relatively low monomer concentration (<1.46 mol·dm^{-3}) were appeared. It was shown that the value of the positive dynamic effect in DBCs syntheses at the same monomer concentration was grows with increase of the MOPEO block (matrices) length.

The synthesized block copolymers were stimuli responsive copolymers. At low pH (pH ≤ 4) PAAc blocks were protonated and connected with chemically complementary MOPEO/PEO blocks. Due to this, block copolymer macromolecules self-assembled into the micelles of different construction and shape. The existence of such micelles with low size distribution in copolymer solutions at pH = 2.5 was fully confirmed by TEM. It was revealed that DBCs and TBC micelles contained a dense hydrophobic "core" and developed "corona". The space of developed "corona", which depended on relative length of nonionic and polyacid blocks, defined a general size of micelles.

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